

EFFECT OF PRESSURE ON POLYMERIZATION PERFORMANCE AND PRODUCT PROPERTIES IN COPOLYMERIZATION OF VINYL/DIVINYL MONOMERS IN CARBON DIOXIDE AT SUPERCRITICAL CONDITIONS

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Abstract - A mathematical model for the free-radical copolymerization kinetics with crosslinking of vinyl/divinyl monomers in carbon dioxide at supercritical conditions is described, and illustrated for styrene/divinylbenzene. The effects of the kinetic and physical parameters on monomer conversion, molecular weight development, copolymer composition, appearance of the gelation point, gel fraction and average cross-link density were studied. Model predictions show the expected trends. It was found that the effect of pressure is particularly important especially at low pressures (near the critical point of CO₂).

Introduction

The literature on polymer chemistry in scCO₂ is extensive and keeps growing, as evidenced from the review by Kendall et al.¹ However, the modeling of polymerization processes in fluids at supercritical conditions has not received much attention to date. To the best of our knowledge, the only two papers that report the comprehensive modeling of free-radical dispersion homopolymerization of methyl methacrylate, MMA, in scCO₂ come from the groups of Kiparissides² and Morbidelli³. Although very few mathematical models on the polymerization of vinyl monomers in scCO₂ are available, systematic studies of this type of process, from an engineering perspective, are starting to appear, as evidenced from the recent experimental study by Rosell et al.⁴, on the effect of mixing on polymerization rate and molecular weight development.

Crosslinked polymers (polymer networks) are very important in technology, medicine, biotechnology, agriculture, and other important areas. They are used as construction materials, paints and coatings, polymer glasses with high mechanical strength and high thermal stability, rubbers, ion-exchange resins and sorbents, insoluble polymer supported reagents, controlled drug-release matrices, electronics and cabling, food packaging, sensors, “smart” materials, artificial organs, implants, superabsorbent materials, and so on.

Due to the very important scientific and technological applications of polymer networks, and the several scientific and technological challenges needed to be addressed in order to produce polymer networks from vinyl/divinyl copolymerization in scCO₂ in a more effective way, the attention of our group was focused into this topic. The copolymerization of styrene and divinylbenzene (DVB) in scCO₂ was chosen as model system. The objective of our group in this contribution was to develop a sound mathematical model that can be able to simultaneously predict, for the first time in this area, overall conversion, copolymer composition, molecular weight development, appearance of the gelation point, gel fraction evolution, and average crosslink density, as function of the system's pressure and temperature.

Modeling

The mathematical model used in this contribution has been described in detail by Quintero-Ortega et al.⁵ The model consists of fifteen ordinary differential equations (ODEs), one for overall initiator consumption, one for overall conversion, two for conversion on each phase, six for moments of the dead polymer, three in each phase, one for divinyl monomer mol fraction, two for crosslink density, one for each phase, one for overall transfer agent, and one for overall inhibitor; six nonlinear algebraic equations for the different radical types, three in each phase, and a number of explicit algebraic equations, such as the ones for the moments of the living polymer population.

Results and Discussion

Although the effect of several process variables and model parameters on the polymerization performance and product properties were analyzed for this contribution (see the details in ref 5), one of the most interesting results obtained is related to the effect of pressure on the behavior of the polymerization, and the properties of the produced polymer, shown in Figures 1 to 4. It is clearly observed that increasing pressure in the region well above the critical point of CO₂ (300-500 bar) causes a modest increase in polymerization rate. However, if pressure is increased in the region closer to the critical point (75-200 bar), the increase in polymerization rate is remarkable (Figure 1). Of course this effect is also reflected on the appearance of the gelation point, as shown in Figure 2.

The gelation point is modestly anticipated when pressure is increased in the high pressure range, but it can be easily tuned within a range of almost 2 hours in the pressure range closer to the critical point of CO₂. The amount of gel produced is almost 100% in most of the profiles analyzed (only in the profile at 75 bar, a limiting value of gel fraction of approximately 95% is observed). It is observed in Figure 3 that although the gelation point can be moved within a time period of two hours (when the total reaction time is not higher than 6 hours, in the slowest system), the crosslink density does not change too much. Even though the average crosslink density did not change much, the crosslinking density distribution (not calculated with our model), i.e., the homogeneity of the polymer network, might change significantly, since Cooper et al.^{6,7} and Hebb et al.⁸ experimentally found that the pore size and surface area of porous crosslinked poly(methacrylate) monoliths synthesized in scCO₂ could be fine-tuned by changing the density of carbon dioxide, namely, by changing the pressure of the polymerization system. The remarkable effect of pressure on the gelation point is also observed in the molecular weight development profile, Figure 4. This situation makes a promising way of significantly change production time, moving to safer operational conditions, without significantly changing the properties of the produced polymer.

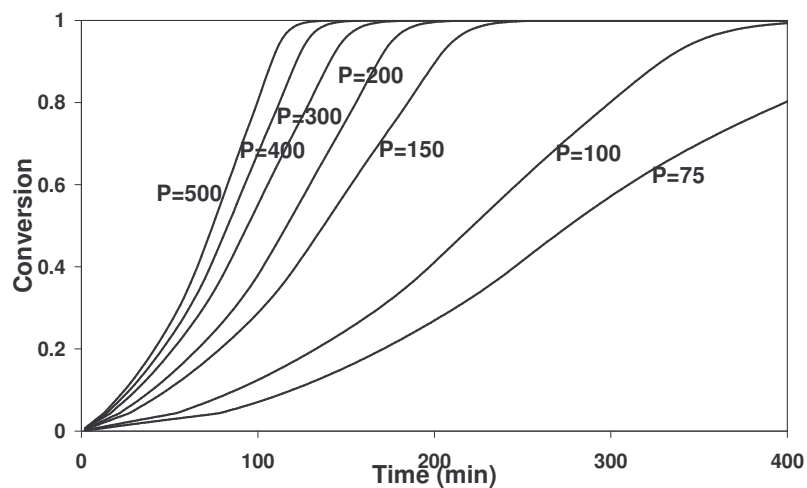


Figure 1. Effect of the operating pressure, P , on polymerization rate.

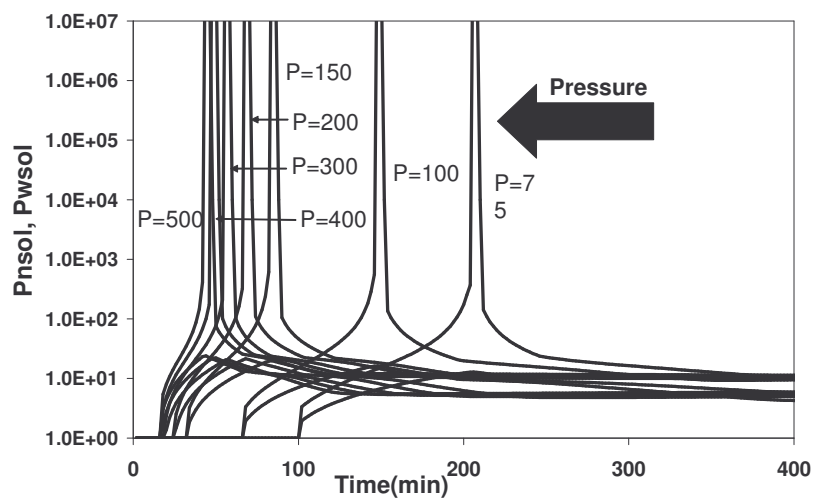


Figure 2. Effect of the operating pressure, P , on number and weight average chain lengths.

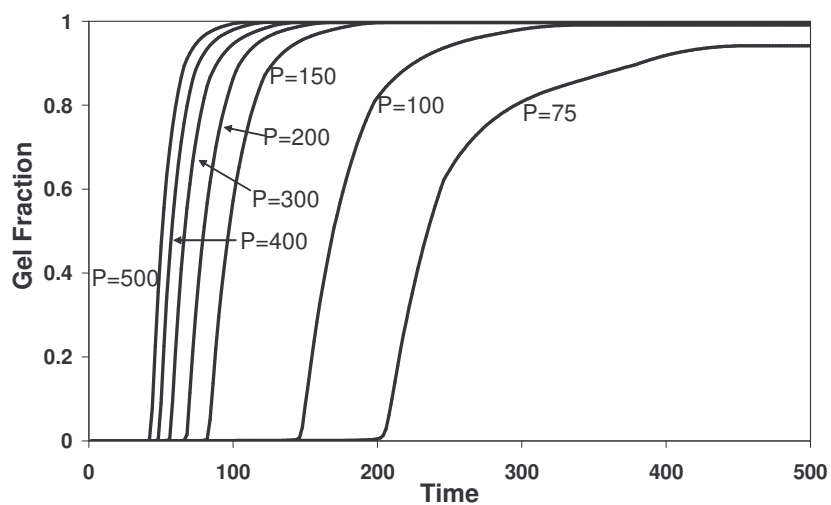


Figure 3. Effect of the operating pressure, P , on gel fraction.

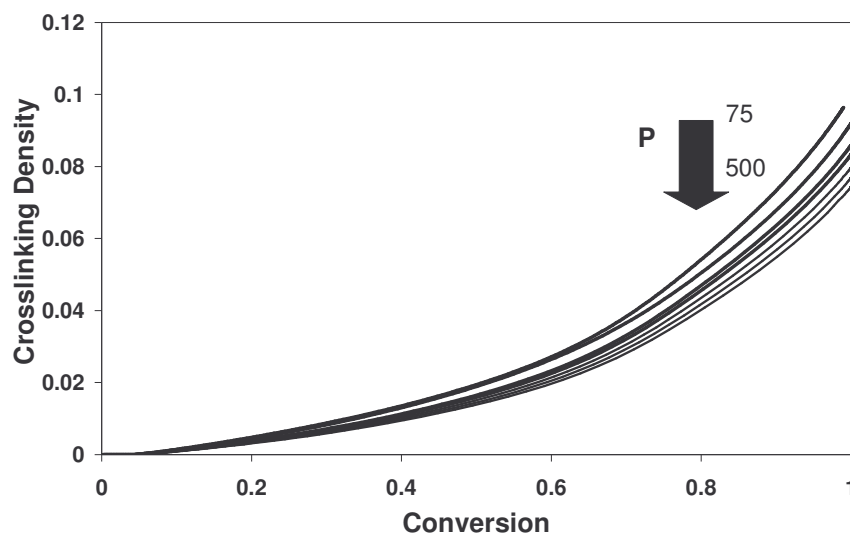


Figure 4. Effect of the operating pressure, P , on crosslink density.

Concluding Remarks

The effects of the recipe (crosslinker content, overall monomer content, and initiator concentration), and the operation conditions (temperature and pressure) on the studied responses mentioned above have been carefully analyzed in our group⁵. It was found the effect of pressure is particularly important. If the system is operated at the same conditions of the experimental studies reported in the literature (well above the critical point of CO_2), the changes that can be obtained in productivity and polymer properties by changing the process conditions and formulation are modest. However, if one moves to lower pressures, closer to the critical point of CO_2 , the model predicts quite significant changes of polymerization rate and appearance of the gelation point, without severely changing the average crosslink density of the produced polymer network

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